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New Physical Interpretation for Time in Scattering Theory

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We show that the collision time may be interpreted as the time average of a flux-flux correlation function. This interpretation leads quantum mechanically to a complex time whose real part is identical to the usual definition as provided by F. T. Smith. The imaginary part is identical, in the semiclassical limit, to the imaginary time associated with tunneling.

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The classical mechanical definition of the duration of a collisional event is straightforward. One measures the time it takes the particles to move from one point in space to another. Quantally, of course, the uncertainty principle prevents such a simple determination. However, as shown by Bohm,[1] Eisenbud,[2] and Wigner,[3] one may extract a time delay associated with the energy derivative of the phase shift. For a multichannel collision at energy E, described by an energy-dependent S matrix with elements S_{ij}, the time delay Δt_{ij} associated with a transition from initial state i to final state j is

$$\Delta t_{ij} = \mathrm{Re}[-i\hbar (S_{ij})^{-1} dS_{ij}/dE]. \tag{1}$$

This relation is based on a wave-packet analysis, which shows that the time delay is essentially the excess time of the collision due to a nonzero potential.

Alternatively, one may define the duration of the collision from a kinetic point of view. Given the density of particles in the interaction region and the total incoming flux, it is obvious, classically, that the average time spent by all incoming particles in the interaction region is just the ratio of the density to the flux. The density and flux are well defined quantally, and so we can use this precription to define a quantal time. In a classic paper, Smith[4] has shown that the kinetic definition and the one given in Eq. (1) are essentially identical. He constructed a collision lifetime operator Q whose diagonal elements give the average time delay from a given initial state. Furthermore, the trace of the operator is just the excess density of states due to the interaction potential. In recent years, Wardlaw, Brumer, and Osborne[5] have generalized Smith's definition to general reactive, multichannel collisions.

In a totally different context, there has been renewed interest in the old question of how much time it takes a system to tunnel through a potential energy barrier. The interest in the tunneling time scale stems from an attempt to understand the effect of additional degrees of freedom on the tunneling probability.[6,7] If the time scales of the "bath" degrees of freedom are much faster or much slower than the tunneling time, one could resort to adiabatic or sudden approximations.[8]

Recently, in a stimulating paper, Büttiker and Landauer[9,10] have suggested that the relevant tunneling time scale is *not* the time delay as defined in Eq. (1). Rather, they show that the tunneling time scale which is important in relation to bath degrees of freedom is the semiclassical imaginary time obtained from the traversal time on the inverted barrier. They suggest that tunneling is a two-time-scale process. One is the real time as determined by Eq. (1); the other is an imaginary time—which is relevant for understanding the effect of the bath degrees of freedom. Stevens[11] has suggested that the imaginary time is just the signal velocity of a wave packet.

It is tempting to identify Büttiker and Landauer's traversal time as

$$\mathrm{Im}\, t_{ij} = \mathrm{Im}\left(-i\hbar S_{ij}^{-1}\frac{dS_{ij}}{dE}\right) = -\frac{\hbar}{2}\frac{d}{dE}\ln|S_{ij}|^2. \tag{2}$$

Semiclassically this reduces to the semiclassical imaginary time. However, a physical interpretation of Eq. (2) is not readily available.

The time shows up in a seemingly totally different context in collision theory. In recent years, much attention has been focused on the definition of rate constants and reaction probabilities as time integrals of flux-flux correlation functions. Chandler[12] and Grote and Hynes[13] have studied the classical mechanical aspects while Costley and Pechukas,[14] and Miller, Schwartz, and Tromp,[15] have studied quantum mechanical properties. Of course, the time appears explicitly in a correlation function and it would seem to be reasonable to define a collision time as the average duration of correlations. However, it is not clear *a priori* whether there is any connection between such a correlation time and the physical classical or quantal time delays.

In this paper, for systems with one degree of freedom, we show that classical mechanically the time average of the flux-flux correlation function is exactly the classical collision time. We then show that the time average of the real part of the quantal microcanonical flux-flux correlation function is the usual time as defined by Smith [and Eq. (1)], while the time average of the imaginary part reduces to the definition in Eq. (2).

We will deal with a one-dimensional scattering problem with Hamiltonian

$$H = p^2/2m + V(x). \qquad (3)$$

The potential $V(x)$ is assumed to have a single barrier with height V_0 and goes to a constant as $x \to \pm\infty$ (for simplicity, at least as fast as x^{-2}). The flux $\bar{F}(x_0)$ at point x_0 is defined classically as

$$\bar{F}(x_0) = (p/m)\delta(x - x_0). \qquad (4)$$

The microcanonical flux-flux correlation function (ffcf) for flux at x_1 at time $t=0$ and at x_2 at time t at energy E is defined as

$$C(x_1,x_2,t;E) = 2\pi\hbar\, \mathrm{Tr}[\bar{F}(x_2(t))\bar{F}(x_1(0))\delta(E - H)]. \qquad (5)$$

For the scattering problem at hand one may define four different ffcf's:

$$C_{aa}(t,E) = \lim_{\substack{\epsilon \to 0 \\ x_1 \to -\infty}} C(x_1,x_2,t;E), \quad x_2 = x_1 + \epsilon,$$

$$C_{ab}(t,E) = \lim_{\substack{x_1 \to -\infty \\ x_2 \to +\infty}} C(x_1,x_2,t;E),$$

$$C_{bb}(t,E) = \lim_{\substack{\epsilon \to 0 \\ x_2 \to +\infty}} C(x_2,x_1,t;E), \quad x_1 = x_2 - \epsilon, \qquad (6)$$

$$C_{ba(t,E)} = \lim_{\substack{x_1 \to -\infty \\ x_2 \to +\infty}} C(x_2,x_1,t;E).$$

Finally one may define a global ffcf

$$C(t,E) = C_{ab}(t,E) + C_{ba}(t,E) - C_{aa}(t,E) - C_{bb}(t,E). \qquad (7)$$

We will prove that both classically and quantally

$$\mathrm{Re}\int_0^\infty dt\, tC(t,E) = 2\pi\hbar\, \mathrm{Tr}\delta(E - H). \qquad (8)$$

Classically, for $E < V_0$, clearly $C_{ab} = C_{ba} = 0$ while

$$C_{aa}(t,E) = \lim_{x_i \to -\infty} [\delta(t) - \delta(t - \tau_{ii}^E)], \qquad (9)$$

where τ_{ii}^E is the time it takes the trajectory initiated at x_i to return to x_i, and a similar relation holds for $C_{bb}(t,E)$. The minus sign is easily seen to come as a result of the reflection—the flux of reflected particles is of opposite sign to those of incoming particles. For $E > V_0$ one finds that

$$C_{aa}(t,E) = C_{bb}(t,E) = \delta(t),$$

$$C_{ba}(t,E) = C_{ab}(t,E) = \lim_{\substack{x_i \to -\infty \\ x_j \to +\infty}} \delta(t - \tau_{ij}^E), \qquad (10)$$

where τ_{ij}^E is the time it takes the trajectory initiated at x_i to reach x_j. Combination of Eqs. (6), (7), (9), and (10) leads[16] to the desired result—Eq. (8).

Deriving the same result quantally is straightforward but more tedious. Quantally, the flux operator is defined as

$$\bar{F}(x_0) = \tfrac{1}{2}[(\hat{p}/m)\delta(\hat{x} - x_0) + \delta(\hat{x} - x_0)\hat{p}/m], \qquad (11)$$

where $\hat{x},\hat{p}$ are the position and momentum operators. The flux operator at time t, $F(x_0(t))$, is given in the Heisenberg representation as

$$F(x_0,t) = e^{iHt/\hbar}\bar{F}(x_0)e^{-iHt/\hbar}. \qquad (12)$$

With this notation the definitions of the ffcf's given in Eqs. (5) and (6) hold also quantally. To proceed, we note that the Hamiltonian H has a set of eigenfunctions $\psi_k(x)$, at energy $E = \hbar^2k^2/2m$, normalized such that

$$\int_{-\infty}^{\infty} dx\, \psi_k(x)\psi_{k'}^*(x) = \delta(k' - k),$$

$$\int_{-\infty}^{\infty} dk\, \psi_k(x)\psi_k^*(x') = \delta(x' - x). \qquad (13)$$

We use the notation

$$\langle\psi_{\pm k'}|\bar{F}(x)|\psi_{\pm k}\rangle \equiv F_{k',k}^{ij}(x), \quad i = +,-, \quad j = +,-. \qquad (14)$$

One may now write the ffcf explicitly as

$$C(x_1,x_2,t;E)=\frac{2\pi m}{\hbar|k|}\exp(ik^2\tau)\int_0^\infty dk'\exp(-ik'^2\tau)\sum_{\substack{j=+,-\\ i=+,-}} F^{i,j}_{k',k}(x_1)F^{j,i}_{k,k'}(x_2). \tag{15}$$

Here the reduced time τ is defined as $\tau=\hbar t/2m$. To prove Eq. (8) one needs the following (standard) results:

$$\int_0^\infty dt\, t\exp[i(k^2-k'^2)\tau]=-(2m/\hbar)^2[(k^2-k'^2)^{-2}+i\pi(d/dk^2)\delta(k^2-k'^2)], \tag{16}$$

$$F^{i,j}_{k',k}(x_2)-F^{i,j}_{k',k}(x_1)=\hbar i/2m(k^2-k'^2)\int_{x_1}^{x_2}dx\,\psi^{*i}_{k'}(x)\psi^{j}_{k}(x),\quad i,j=+,-;\,-,+. \tag{17}$$

Equation (17) may be obtained by first taking the position derivative of $F^{i,j}_{k',k}(x)$, using the Schrödinger equation for ψ_k explicitly, and then integrating. We also need the algebraic identity

$$\begin{aligned}F_{k'k}(x_1)F_{kk'}(x_2)+F_{k'k}(x_2)F_{kk'}(x_1)&=|F_{k'k}(x_1)|^2+|F_{k'k}(x_2)|^2\\&\quad-[F_{k'k}(x_2)-F_{k'k}(x_1)][F_{k,k'}(x_2)-F_{kk'}(x_1)].\end{aligned} \tag{18}$$

Equations (15) and (16) imply that

$$\begin{aligned}&\operatorname{Re}\int_0^\infty dt\,t[C(x_1,x_2,t;E)+C(x_2,x_1,t;E)]\\&\quad=-\left(\frac{2m}{\hbar}\right)^2\frac{2\pi m}{\hbar|k|}\int_{-\infty}^{\infty}dk'(k^2-k'^2)^2\{[F_{k'k}(x_1)F_{kk'}(x_2)+F_{k',-k}(x_1)F_{-k,k'}(x_2)]+\text{c.c.}\}.\end{aligned} \tag{19}$$

Note though that $F^*_{k'k}=F_{kk'}$; thus one may use Eqs. (17) and (18) to find that

$$\begin{aligned}\operatorname{Re}\int_0^\infty dt\,t[C(x_1,x_2,t;E)+C(x_2,x_1,t;E)]&=\pi\hbar(m/\hbar^2|k|)\{\int_{x_1}^{x_2}dx[|\psi_k(x)|^2+|\psi_{-k}(x)|^2]\}\\&\quad+\operatorname{Re}\int_0^\infty dt\,t[C(x_1,x_1,t;E)+C(x_2,x_2,t;E)].\end{aligned} \tag{20}$$

Equation (8) follows immediately.

We have thus shown that the time average of the real part of the microcanonical ffcf reduces to the usual definition for the collision time. Of course, classical mechanically, $C(t,E)$ is real. However, quantally the ffcf is complex so that one may evaluate the time average of the imaginary part. To do so we first note the following identity:

$$\operatorname{Re}\int_0^\infty dt\,C(x_1,x_2,t;E)=\pi\hbar 2\pi\hbar\operatorname{Tr}[\bar F(x_1)\delta(E-H)\bar F(x_2)\delta(E-H)]\equiv N(E), \tag{21}$$

which is easily obtained by direct integration of the quantal version [cf. Eq. (12)] of Eq. (5). One may take the derivative of Eq. (21) with respect to either x_1 or x_2 to see with the aid of Eq. (17) that $N(E)$ is truly independent of x_1 and x_2. Furthermore, for $x_1=x_2$, Miller, Schwartz, and Tromp[15] have shown that $N(E)$ is just the transmission probability at energy E. Thus, Eq. (21) is an expression of flux conservation—the net flux passing a point integrated over all time is the same irrespective of the location of the point.

To obtain the imaginary time average one uses Eqs. (15)-(18) to find that

$$\begin{aligned}\operatorname{Im}\int_0^\infty dt\,t[C(x_1,x_2,t;E)+C(x_2,x_1,t;E)]&=2\hbar(\pi\hbar)^2\operatorname{Tr}\{[\bar F(x_1)\delta(E-H)\bar F(x_1)(d/dE)\delta(E-H)\\&\quad+\bar F(x_2)\delta(E-H)\bar F(x_2)(d/dE)\delta(E-H)]\}.\end{aligned} \tag{22}$$

Use of Eq. (21) immediately gives

$$\operatorname{Im}\int_0^\infty dt\,t[C(x_1,x_2,t;E)+C(x_2,x_1,t;E)]=\hbar\,dN/dE. \tag{23}$$

We now define an imaginary time as

$$\langle t\rangle_{\text{im}}\equiv\frac{\operatorname{Im}\int_0^\infty dt\,t[C_{ab}(t,E)+C_{ba}(t,E)]}{\operatorname{Re}\int_0^\infty dt[C_{ab}(t,E)+C_{ba}(t,E)]}=\frac{\hbar}{2}\frac{d}{dE}\ln N(E). \tag{24}$$

Clearly $\langle t \rangle_{\mathrm{im}}$ is identical with the imaginary time defined in Eq. (2).

In summary, we have shown that the time of a collision may be interpreted as an average correlation time. In quantal systems, the time is complex; the real part gives the actual duration of the collision, and the imaginary part is significant for systems with more than one degree of freedom.[9,10] Generalization of these results to multidimensional systems as well as applications to quantal transition state theory and bimolecular reactive scattering will be considered in detail in forthcoming work.[17]

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